Sedimentology of Pleistocene palustrine tufas and associated deposits of the Ebrón Valley (Iberian Ranges, Spain)

Sedimentología de las tobas palustres pleistocenas y depósitos asociados del Valle del Ebrón (Cordillera Ibérica, España)

Stephen Ajuaba¹, Concha Arenas^{2,*}, Enrico Capezzuoli³

³Department of Earth Sciences, University of Florence, Via La Pira 4, 50121 Firenze, Italy. ORCID ID: http://orcid.org/0000-0002-4199-1870

* Corresponding author: carenas@unizar.es

ABSTRACT

Extensive palustrine tufa deposits are not common in the geological record, in part due to their liability to erosion. This work discusses the formation and preservation factors that allow the wide development of such facies, taking the example of a Middle-Late Pleistocene dominantly palustrine area that formed downstream of a high-slope stepped tufa fluvial stretch, in the Ebrón river Valley (south Iberian Range). The study case (Los Santos area) consists of coarse detrital sediments at the base, associated with pronounced incisions on the underlying deposits, followed by a variety of tufa and associated carbonate facies, with a minimum thickness of 19 m. The most abundant facies are the phytoclastic rudstones, carbonate sands and silts with gastropods and ostracods and up-growing stem boundstones. Less common are moss boundstones, down-growing stem boundstones and bioclastic limestones. Up to five simple vertical sequences of facies (facies associations) are characterized. The sedimentary facies model corresponds to a low-slope and wide stretch at the end of a stepped, cascade-barrage fluvial system, with extensive palustrine areas, shallow ponded areas, at places with stagnant conditions, and small cascades. Variations of bedrock lithology, from Mesozoic carbonate rocks upstream to Neogene alluvial rocks downstream, allowed the gentle sloping and wide low-layering surface at the distal termination of the fluvial system, with overall low-energy facies, which supports the absence of stromatolites. Indeed, the lack of vigorous erosional processes enabled a dense cover of hydrophilous plants to thrive on diverse environments and the accumulation and preservation of organic matter. The small thickness of the studied deposits, compared to that of upstream deposits, is consistent with a reduction of dissolved calcium and bicarbonate contents downstream (linked to the distal position from the carbonate aquifer sourced springs), and with the diminishing mechanical CO,-degassing in low-gradient environments.

Keywords: Palustrine tufa; low-energy deposition; facies model; Pleistocene; Iberian Ranges

Citation / Cómo citar este artículo: Ajuaba, S. et al. (2021). Sedimentology of Pleistocene palustrine tufas and associated deposits of the Ebrón Valley (Iberian Ranges, Spain). Estudios Geológicos 77(1): e137. https://doi.org/10.3989/egeol.44131.593

¹ Chair of Petroleum Geology. Department of Applied Geosciences and Geophysics. Montanuniversitaet Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria. ORCID ID: https://orcid.org/0000-0001-5748-7284

² Stratigraphy Division. Science Faculty, Geotransfer and IUCA, University of Zaragoza. C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain. ORCID ID: http://orcid.org/0000-0002-4212-0524

Recibido el 26 de octubre de 2020; Aceptado el 4 de febrero de 2021; Publicado online el 20 de mayo de 2021

Copyright: © 2021 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution- Non Commercial (by-nc) Spain 4.0 License.

RESUMEN

En el registro geológico, los depósitos de tobas palustres extensos no son comunes. Este trabajo discute los factores para la formación y conservación de extensos depósitos palustres, tomando como ejemplo los depósitos del Pleistoceno medio-superior que se formaron en el tramo distal del sistema de tobas fluviales del río Ebrón (Cordillera Ibérica, en Teruel y Valencia). Los depósitos estudiados (área de Los Santos) constan de sedimentos detríticos en la base, asociados a incisiones fluviales profundas sobre el sustrato, seguidos por una sucesión de carbonatos con amplia variedad de facies tobáceas, con un mínimo de 19 m de espesor. Las facies más abundantes son los rudstones fitoclásticos, arenas y limos de carbonato con gasterópodos y ostrácodos, y los boundstones de tallos de plantas creciendo hacia arriba. Menos comunes son los boundstones de musgos y de tallos colgantes, y las calizas bioclásticas. Hasta cinco secuencias verticales de facies se han caracterizado. El modelo de facies corresponde al tramo al final de un sistema tobáceo fluvial escalonado con cascadas-barreras, en el que se formarían extensas áreas palustres, áreas encharcadas someras, algunas con estancamiento, y pequeñas cascadas. Las variaciones litológicas del sustrato pre-Cuaternario, desde rocas carbonáticas aguas arriba a rocas aluviales aguas abajo, permitió la formación de esa superficie amplia y de poca pendiente al final del sistema fluvial escalonado, en conjunto con facies de poca energía, lo cual apoya la ausencia de estromatolitos. Además, la escasez de procesos erosivos intensos permitiría que una densa cubierta de plantas hidrófilas prosperara en diversos ambientes, así como la acumulación y conservación de materia orgánica. El escaso espesor de la secuencia estudiada se relaciona con la disminución del contenido en calcio y bicarbonato disueltos en el agua (por la situación distal respecto a las fuentes alimentadas por el acuífero carbonatado) y la disminución de la intensidad de desgasificación de CO, en ambientes de poca pendiente.

Palabras clave: Tobas palustres; depósitos de baja energía; modelo de facies; Pleistoceno; Cordillera Ibérica

Introduction

Tufas are continental calcium carbonates, mainly calcite, forming in ambient-temperature water rich in dissolved calcium (Ca^{2+}) and bicarbonate (HCO_{2-}) ions. These terrestrial carbonates mainly form by calcite precipitation on biotic substrates in a large variety of depositional environments, mainly through the CO₂ loss from water, either caused by changes in temperature, biological processes or mechanical turbulence (Pentecost, 2005). Tufas are common features in mostly freshwater carbonate rivers and lakes, but also in saline and alkaline lakes (Pentecost, 2005; Della Porta, 2015). These carbonates are characterised by a distinct range of sedimentary facies (based on textures, structures and geometry features), and petrophysical and geochemical properties (Capezzuoli et al., 2014). They encompass a wide array of sedimentary facies, whose abundance and/or spatial distribution through a given system depend on factors such as the hydrodynamics, water discharge and topography of the sedimentation zones, mostly the slope along the river profile (Violante et al., 1994; Viles & Pentecost, 2007; Arenas-Abad et al., 2010; Arenas et al., 2014a; among others).

During the Quaternary, tufas developed primarily during the interglacial periods, *i.e.* correlative with

the odd Marine Isotope Stages (MIS; e.g., Gibbard et al., 2005). In mid latitude regions these deposits were conspicuous approximately 100 ka ago, *i.e.* during MIS 5 (Sancho et al., 2015). Many studies on tufa have focused on their palaeoclimatic implications, since their formation would appear to be particularly favoured in warm (Henning et al., 1983; Durán, 1989; Martín Algarra et al., 2003) or humid conditions (Capezzuoli et al., 2010). However, the deposition of tufa has been detected to occur through a wide range of climatic conditions from temperate-wet to semi-arid (Auler & Smart, 2001; Viles et al., 2007; Cremaschi et al., 2010; Moeyersons et al., 2006). Therefore, climate would not appear to be the only factor influencing their formation (Viles & Pentecost, 2007). Rather, other factors such as topography of the basin, bedrock lithology and associated aquifer characteristics, may all influence tufa formation (Arenas-Abad et al., 2010).

Facies models for most Quaternary fluvial tufa systems include a variety of environments such as cascades, barrage-cascades, dammed water areas along the channels, pools in the floodplain and palustrine areas, which are variably developed through the stepped systems depending on each case (*e.g.*, determined by high to moderate slope). In the literature, extensive palustrine areas have not been commonly described in association with stepped fluvial systems, with the exception of a few examples (Pedlev et al., 2003; Özkul et al., 2010). The work presented herein is an exception of this rarity: it describes the case of a wide, dominantly palustrine area that developed downstream of a high-slope stepped fluvial stretch. The rarity of extensive tufa palustrine deposits could be related to their liability to erosion, as these facies would be reworked into other tufa deposits. Moreover, the fact that most stepped systems have limited extent to allow palustrine areas to be developed indicates that the width and topography of the fluvial basin also account for the development and preservation of palustrine deposits. Therefore, extensive palustrine deposits are expected to be developed and preserved at the most downstream zones of the fluvial system, coinciding with decrease in slope, and/or at the latest fill stages of the basin.

This work presents a study of the tufa and associated deposits in the Quaternary Ebrón river Valley (Teruel and Valencia, Spain), focussing on a portion of the Pleistocene record located at the downstream stretch, *i.e.*, at the Los Santos area, in which palustrine facies dominate. The purpose of this work included: 1) Stratigraphic and sedimentological characterization of the fluvial tufa system and their associated deposits generated during the Middle-Late Pleistocene; 2) Construction of a conceptual sedimentary facies model of the tufa system and its comparison with other examples. The obtained results can be used for comparative studies with other Mediterranean nearby tufa systems, as well as with other distant tufa systems of a similar or different time span.

Geographical and geological context

The study area is localized in the Iberian Range, an intra-plate range formed during the Alpine orogeny in the north-eastern part of the Iberian Peninsula (Fig. 1). The area is within the "National Topographic Map" n. 612 (Ademuz), 1:50000, of the *Instituto Geográfico Nacional* of Spain. The studied Quaternary record is part of a series of deposits cropping out along the present Ebrón river Valley. This river, a tributary of the Turia River, is 42 km long and flows from northwest (1370 m a.s.l) to southeast (730 m a.s.l). The Turia River enters the Mediterranean Sea in the city of Valencia. The Ebrón River basin occupies a drainage area of 245 km² with altitude ranging between 1723 and 730 m a.s.l. (Arenas *et al.*, 2015).

From north to south, the bedrock across which the Ebrón River flows is composed of several units (Fig. 2): Lias-Dogger limestones and dolostones affected by faults oriented in a NE-SW to N-S direction, Triassic dolostones (Muschelkalk Facies) and strongly folded gypsum-rich mudstones (Keuper Facies), south-dipping Upper Cretaceous limestones and dolostones and, further south, sub-horizontal, mostly detrital Miocene rocks of continental origin. The Quaternary tufa deposits crop out along the terraced valley fill as discontinuous geological bodies that have been cut across by the river as it flows downstream; these geobodies are formed mainly of carbonate deposits and associated minor clastic deposits (*i.e.*, formed of extraclasts), for a length from Castielfabib to Los Santos villages (Lozano et al., 2012).

Previous studies on the Quaternary deposits of the Ebrón river Valley focussed on mapping, stratigraphy and preliminary sedimentology (Sancho *et al.*, 2015). Chronological data have been obtained from amino acid racemization, radiocarbon analysis and U/Th series (Lozano *et al.*, 2012; Sancho *et al.*, 2015). These results showed that tufa deposition occurred during MIS 6 and MIS 5 (180–100 ka), and MIS 1 (6–2 ka). Evidence of older tufa deposits (*i.e.*, MIS 13, 490 ka) was found from reworked material included in the studied sections, but the corresponding in situ deposits are not present in the outcropping record. Therefore, two main units are present (Figs. 2 and 3).

1) Middle–Late Pleistocene deposits consisting of conglomerates, carbonate sands and silts, stromatolites, phytoclastic, up-growing stem and bryophyte limestones, and speleothems that crop out at sections "c" (Cascada) and "d" (Mirador) (Fig. 2). Thickness is approximately 77 m in section "d" (Fig. 3B, C).

2) Holocene deposits consisting of carbonate sands and silts, bryophyte, phytoclastic and up-growing stem limestones, and stromatolites, that crop out at sections "a" (Convento) and "b" (Central) (Fig. 2). Thickness is approximately 25 m in section "a", but reaches up to 50 m down to the present river course (Fig. 3A, C).



Figure 1.— Location of the studied area in the northeast of the Iberian Peninsula. A) Geographic location. B) Geological location of the Ebrón river Valley in the Iberian Range. Geological map of the Iberian Peninsula, Balearic Islands and Canary islands. Scale 1:1000000. *Instituto Tecnológico y Geominero de España* and *Instituto Geológico e Mineiro de Portugal*. Madrid. Adapted from Álvaro *et al.* (1994).

The downstream area of Los Santos, related to the upstream Pleistocene deposits, has been of interest for investigation, given reason for this study (Fig. 4). No absolute dating for the Los Santos rocks has been performed. However, from previous works of Lozano *et al.* (2012) and Sancho *et al.* (2015) on the Castielfabib outcrops, correlative comparison between Los Santos and the middle-upper part of Castielfabib section will date Los Santos to Middle–Late Pleistocene.

Materials and methods

Three stratigraphic sections (LSAN-1, 2 and 3, located in Fig. 2) were measured and correlated as

presented in figure 5. Several other outcrops were also considered (*e.g.*, deposits close to and in the village of Los Santos). This correlation was established physically through a conspicuous traceable organic rich layer, the general presence of coarse detritals at the base and by following other stratigraphic levels in the field. From the measured sections, 35 different samples were collected for analysis of their textural features, including mineralogy. 30 thin sections were prepared for petrographic microscope observation, and 6 samples having different facies for scanning electron microscope (SEM) at the Electron Microscopy Service of the *Servicio de Apoyo a la Investigación* (SAI) of the University of Zaragoza (Spain). Thin sections were perfomed at the *Servi*-



Figure 2.— Geological map of the study area from Sancho *et al.* (2015), with location of stratigraphic sections. a, b, c, d: Stratigraphic sections of Sancho *et al.* (2015). 1, 2, 3: Stratigraphic sections of this work.

cio General de Preparación de rocas y materiales duros of the SAI. Ten mudstone and marly samples were analysed for calcium carbonate content using a manocalcimeter (Geoservices, France) based on the Scheibler method, available at the Stratigraphy laboratory of the University of Zaragoza (Spain).

Herein, the codes of classification of Miall (1978) have been used for the clastic facies (*i.e.*, formed of extraclasts), and the codes of classification of Arenas-Abad *et al.* (2010) have been used for the carbonate facies (Table 1). The term "palustrine" is used here to refer to shallow water zones with hydrophilous vegetation, in which the submerged portions of plants are coated by calcite. In the context of fluvial tufa systems, water level fluctuations are not as relevant as in the case of close lacustrine systems, which differs from the use of the term by Freytet & Plaziat (1982) in the lacustrine environments.

Stratigraphy

The studied deposits in the Los Santos area (Figs. 2, 4, 5 and 6) are dominated by limestones over clastic sediments (*i.e.*, consisting of extraclasts). The record showed a small proportion of polymictic clastic deposits composed of conglomerates, sandstones

and occasionally mudstones, overlain by the dominant carbonate deposits that consist of varied sedimentary facies (Figs. 5 and 6). Three stratigraphic sections were measured (Fig. 5). These sections have been divided into several units for the sake of clarity in description. These units are based on lithology and/or textural characteristics. Individual facies description and facies labels in the following summary are found in Table 1.

Section LSAN-1

The section is 6 m thick and divided into 5 units (Figs. 5 and 6A). Unit 1 is 1.9 m thick of alternating tabular siliceous sand and lime mud (Fm, Mm) layers, with interbedded channel-shaped gravel deposits. This unit is fining upward with increasing calcium carbonate content upward. Unit 2 is 1.7 - 2 m thick conglomerates and gravels (Gm, Gt) forming tabular bodies with very irregular erosional base. Unit 3 is 1.55 m thick siliceous and minor carbonate sands alternating with gravel layers, with lenticular and tabular geometry. Unit 4 is formed of a 0.12 m thick tabular body of siltstone, marls and lime mud (Mm, Fm). Unit 5 is a 1.3 m thick, flat base tabular body of tufa limestone consisting of phytoclastic rudstone and up-growing stem boundstone (Lph, Lst 1).

Section LSAN-2

The section is 15 m thick and divided into 8 units (Figs. 5, 6B and 6C). Unit 1 is formed of 1.3 m thick carbonate sands and claved lime mud (Sb, Mm) with intercalated layers consisting of cm-mm phytoclasts and extraclasts. Unit 2 is a 0.26 m thick sand, silt and marlylime mud layer with peaty laminae, with irregular base and top. Unit 3 is a 2 m thick limestone of carbonate sand-packstone, phytoclastic rudstone and up-growing stem boundstone (Sb, Lph, Lst1), with tabular bodies having erosional bases and cross stratification. Unit 4 is formed of 3.7 m thick tufa limestones consisting of alternating phytoclastic and up-growing stem facies (Lph, Lst1) forming irregular and lenticular bodies, and moss boundstones (Lbr) forming dm-thick hemidomic and lenticular bodies. Unit 5 is a 1.2 m thick limestone dominated by up-growing stem boundstones (Lst1). Unit 6 is 2.4 m thick, formed of phytoclastic limestones (Lph, Lphf) and carbonate sands (Sb, Lbg) constituting



Figure 3.— Ebrón Valley field views (A and B) and stratigraphic sections (C) upstream of the Los Santos studied area (see Fig. 2 for location). Section "a" corresponds to the upper 25 m of the 50-m deep cliff. Base of section "d" is not visible in image B). Stratigraphic sections and ages (Marine Isotope Stages - MIS) from Lozano *et al.* (2012) and Sancho *et al.* (2015).



Figure 4.— Field image of the westernmost portion of the Los Santos studied area in the Ebrón river Valley. The studied Pleistocene deposits are light orange and withish in color. Horizontal strata orange in colour are Neogene clastic deposits.

tabular bodies. Unit 7 is 1.5 m thick buried zone, likely buried tufa. Unit 8 is 3 m thick and consists of alternating tabular and lenticular layers formed of phytoclastic and phytoherm limestones (Lph, Lphf, Lst1) and carbonate sand-silt layers (Sb).

Section LSAN-3

The section is 17 m thick and divided into 7 units (Figs. 5 and 6D). Unit 1 is 1.8 m thick of conglomerates and gravels (Gm, Gt) with deeply concave erosional base at the disconformity surface with the Neogene clastic rocks (Fig. 6D). Unit 2 is formed of 2 m thick sandstones. These sandstones form a lenticular body with concave erosional base that shows trough cross-stratification (St), with palaeocurrents toward the south-southwest. Unit 3 is 2.7 m thick tufa limestones (Lph, Lst 1) consisting of lenticular and tabular bodies. Unit 4 is a 2.2 m thick alternation of mudstone (Fm) and lime mud with tabular, phytoclastic rudstone bodies. Unit 5 is 4.5 m thick, but not well exposed, carbonate sands (Sb). Unit 6, 2 m thick, is formed of an isolated build-up formed of moss boundstones (Lbr), phytoclastic rudstones (Lph, Lphf), and phytoherm facies (Lst1, Lst2). Unit 7 is 2 m thick buried material.

Deposits close to and in the village of Los Santos (Fig. 7)

No attempt was made to measure stratigraphic sections given the vertical topography (*i.e.*, cliffs) and/ or poor exposures in this part of the studied area. The deposits close to the village consist of ca. 6 m of thick greyish carbonate sands with interbedded cmthick peaty layers that are recognized over extensive areas, of hectometre lateral continuity, despite most parts being covered, *e.g.*, by fine detritals from younger overlaying sediments (Figs. 7A, 7B, 7C). The deposit outcropping in the village is formed of *ca*. 4 m thick of tufa limestone consisting of conspicuous up-growing stems arranged in extensive palisades cm to dm high and *ca*. 7.5 m visible wide, and associated carbonate sands and phytoclastic tufa (Fig. 7D, 7E). In general, these deposits conform tabular geometries.

Stratigraphic correlation and remarks

Correlation between sections 1 and 2 could be established by visual continuity of beds. Moreover, the presence of a traceable, conspicuous organic-rich layer served as a basis for the recognition of physical correlation between section 1 (unit 4) and section 2 (unit 2) (Fig. 5). This was further supported by correlation of detrital sediments from the bases of the outcrops, as seen in section 1-unit 2 and section 3-unit 1 (Figs. 5, 6A, 6D). Sections 1 and 3 showed a deep concave surface representing incision at the base and then leading to the detrital filling of the channels. Section 3 showed a disconformity relation between the Quaternary rocks and the Neogene rocks (Fig. 6D).

Therefore, at the base of the tufa outcrop, detrital sediments are associated with erosional surfaces, with pronounced incisions of the underlying deposits (Fig. 6A). Units 4, 5 and 6 of section 2 are approxi-



Figure 5.— Stratigraphic sections and correlations in the studied area: LSAN-1, -2 and -3 (see Fig. 2 for location). Explanation in the text.



Figure 6.— (A) Field view of section LSAN-1, with indication of units (as described in the text). Note conglomerates and sandstones at the base, then limestones. (B) and (C) Field views of section LSAN-2, with indication of units. Almost entirely limestone with marks and lime mud at the base. (D) Field view of section LSAN-3 showing disconformity of Pleistocene over Neogene strata. Note the deeply concave, erosive surface that separates the horizontal strata of Neogene detrital deposits (orange-coloured) and Pleistocene conglomerates, sandstones and limestones (beige or whitish-coloured). Legend for facies labels in Figure 5 and Table 1. Units are described in the text.



Figure 7.— Field views of deposits outcropping close to the village of Los Santos (A, B, C) and in the village of Los Santos (D, E). (A, B, C) Dominant carbonate sands with interbedded fine phytoclastic rudstones and peaty layers. Note in A the orange color due to overlying silt dropping. (D, E) Tabular deposits consisting mostly of up-growing stem boundstones, and associated carbonate sand and fine phytoclastic rudstones. Legend for facies labels in Figure 5 and Table 1.



Figure 8.— Field views of diverse carbonate sedimentary facies (Table 1). (A) Fine phytoclastic and intraclastic limestones (Lphf, Li) alternating with banded bioclastic limestones (Lb); Note up-growing stem boundstones at the upper part (Lst1). Partly representing FA 2. (B) Carbonate sands (Sb), phytoclastic limestones (Lphf and Lph) and up-growing stem boundstones (Lst1), forming upper FA 1. (C) Moss boundstones (Lbr) forming lenticular and hemi-domed bodies at the base, followed by up-growing stem boundstone (Lst1) and carbonate sand (Sb), of FA 2 and 4. (D) Detail of FA 2 showing banded bioclastic limestones (Lbr) and phytoclastic and up-growing stem limestones. (E) Detail of C showing layers consisting of up-growing moss stems (Lbr). Note at the base the presence of leaf mounds. (F) Large up-growing stem boundstones (Lst1) laterally and vertically related to bioclastic limestone (Lb), as in FA 2.



Figure 9.— Field views of diverse clastic sedimentary facies formed of extraclasts (Table 1). (A) Conglomerates and gravels (Gm and Gt) and sandstones (St), followed by stem limestones, at the base of FA 1. (B) Detail of heterometric and polymictic gravels, typical at the base of FA 1. (C) Alternating gravel and sand forming cross stratification (Gt, St), in channel fill, then floodplain fines (Fh and Sh). Note small scours at the base of the carbonate deposit (blue arrow). (D) Fine clastics deposited on the floodplain (Sm, Sh, Fh), with small bedforms producing cross stratification (St). Note the passage to marly sediment and then phytoclastic limestones upward. (E) Alternating fine siliciclastic (St, Fh) and mixed sediment (Mm), and phytoclastic limestones (Lph) over carbonate sand (Sb). Note dark grey colour of marls due to fine organic matter content, locally peaty layers (C). (F) Mostly fine siliciclastic deposits (Sh, St) and carbonate sand and marl (Sb, Mm) formed in floodplain, then palisade of up-growing calcite coated stem boundstones (Lst1) (FA 1).



Figure 10.— Field views of diverse peaty and marly sedimentary facies (Table 1). (A) Phytoclast limestones then carbonate sand followed by fine siliciclastic deposits (St, Sh, Fh). (B) Alternating fine siliciclastic (St, Fh) and phytoclastic limestones (Lph) over carbonate sand (Sb). Note dard grey colour corresponding to peaty layers (C), as in FA 1 and 3. (C) Detail of B. (D) Typical deposit of carbonate sand and silt with gastropods (red circles) passing upward to marly and peaty deposits, in outcrops close to the village of Los Santos, representing upper part of FA 3.

mately equivalent to units 4 and 5 in section 3. Thickness measurements in the three sections indicated a minimum thickness of *ca.* 19 m (merged sections 1 and 2) and 17 m (section 3) in the western parts of the outcrop (see Fig. 2 for location), although the contact with bedrock was only exposed in section 3.

Correlation between the deposits close to and in the village of Los Santos (Figs. 4; 5A, 5B, 5C, 5D) and those of section 3 is difficult. It is tentatively proposed that the deposits in the village are equivalent to the interval between meters 5 and 8 (units 3 to 5), and the deposits close to Los Santos are equivalent Table 1.— Main features of the sedimentary facies and interpretation of their depositional sedimentary context in the studied Los Santos area. Interpretation is based on our observations and deductions herein, and information provided by Pedley (1990), Pentecost (2005), Capezzuoli *et al.* (2009), Arenas-Abad *et al.* (2010) and Arenas *et al.* (2014a). Facies nomenclature and abbreviations adapted from Miall (1978)'s code and Arenas-Abad *et al.* (2010)'s code.

| | annieviarioris auapreu ir | UIII IVIIAII (1970) S COUE AIN AIEIIAS-ANAU EL AI. | (zu iu) s cuue. | | | |
|--|---|---|--|---|--------------------------------|---|
| Facies and abundance (Figures) Colour | Geometry of deposits | Microstructure, texture and components | Sedimentary structures | Identifiable biological content | Common associated facies | Depositional sedimentary context |
| Bioclastic limestones. Lb (Figs. 8A, 8C, 8F; 11A) Cream | Tabular and lenticular beds, 0.01 to 0.1 m thick, grouped in tabular sets up to 0.6 m thick. Centimetres to metres in lateral extent. | Mudstones to wackestones of gastropods and other unidentifiable shell fragments. Portions of microbial filament-bearing fan bodies. Commonly peloidal micrite. | Structureless or with horizontal lamination. No root bioturbation. | Gastropods and unidentifiable shell fragments. Microbial filament-shaped bodies. | Lph, Sb and M | Aggradation in slow flowing and ponded areas along the river channel and pools in the floodplain. |
| Carbonate sand and mud. Sb ■■■ (Figs. 6A 6B, 6C; 7A,7B,7C,7D; 11B) 7A,7B,7C,7D; 11B) Cream, light grey to dark grey and locally black | Tabular and lenticular beds, 0.1 to 0.6 m thick, grouped in tabular sets up to 1 m thick. Metres to decametres in lateral extent. | Bioclastic sand and silt. Poorly to slightly lithified, fine to coarse sand and lime mud (mostly silt) carbonate particles; includes gastropods, ostracods and fragments of plants coatings. Commonly peloidal micrite. Microscopic and macroscopic coaly matter in laminae. | Structureless; in some cases, parallel and undulate lamination. | Gastropods, ostracods and plant fragments. | Lph, Lb, M and C | Aggradation in slow flowing and ponded areas along the river channel and pools in the floodplain. Stagnant conditions favouring accumulation and preservation of coaly matter. commonly peat |
| Intraclastic limestones. Li (■) (Fig. 8A) Cream to light brown | Lenticular beds up to 30 cm thick and metres in lateral extent. | Wakestone to rudstone consisting of unsorted intraclasts and other coarse phytoclasts, Unidentifiable carbonate tufa fragments mm to cm long. | Structureless; in some cases with banding. | None, apart from elements within the carbonate grains. | Lph, Lphf, Sb | Small channel fills and floodplain deposits during and after breakage of previous tufa deposits upstream. |
| Phytoclastic tufa. Lph, Very fine stems (mm long): Lphf Iene (Figs. 6A, 6C, 6D; 7E, 8A, 8B, 8C, 8D; 10A, 10B; 11C, 11D) Cream to orange | Tabular, undulate and lenticular beds, 0.1 to 0.3 m thick, grouped in tabular sets up to 1.6 m thick. Decimeters to decameters lateral extent. | Rudstone and packstone of macrophytes: non-organised fragments of calcite-coated stems, mm to cm long, with laminated coating up to 1 cm thick; external moulds of stems and other portions of plants and leaves not preserved; other autochthonous carbonate facies clasts. Laminated coatings formed of light (microspar) and dark (micrite) with filamentous microbial bodies. | Structureless. In a few cases horizontal and undulating layering, also with groups of stems lying parallel to palaeoflow. | Fragments and entire parts of macrophytes (trunks, stems) and leaves. Gastropods. Calcite laminae with calcified filamentous microbial bodies. | Let 1, Lbr, Lphf, Sb | Ubiquitous; Water flow action erodes phytoherm tufas (Lst 1) and associated deposits over palustrine zones, such as trunks and stems, most of them already coated by calcipe, then deposited in floodplains, dammed areas or along active channels, at places as barrage deposits. |
| Phytoherm tufas of: Up- growing stems. Lst 1. == (Figs. 7D, 7E; 8A, 8B, 8C, 8D, 8F; 9F; 11D, 11F) Cream to light brown | Patchy, commonly lenticular bodies, 0.15 to 0.6 m thick, decimeters to meters in lateral extent (if laterally grouped). Tabular and lenticular strata, 0.15 to 1.3 m thick. | Boundstones of vertical stems (up- growing) of macrophytes, coated with laminated calcite. Bunches and palisades of stems up to 40 cm high. In some cases, boundstone of moulds (without coating). Inner diameter from 4 to 6 mm wide. | Structureless | Portions of macrophytes. Calcite laminae with calcified filamentous microbial bodies. | Lbr, Lph, Lphf, Lb | Flooded areas in the floodplains and banks in some channel areas, dammed areas upstream of barrages. Slow- flowing water areas with growth of hydrophilous vegetation and calcite precipitation in the submerged parts of the plants. |

| acies and abundance igures) olour | Geometry of deposits | Microstructure, texture and components | Sedimentary structures | Identifiable biological content | Common associated facies | Depositional sedimentary context |
|--|---|---|--|---|--------------------------------|--|
| toherm tufas of: tains (down-growing ns). Lst 2 am to orange | Curtains (prisms). Commonly forming overhangs 0.01 to 1.5 m thick (high). Decimeters to meters wide. | Boundstones of hanging stems of macrophytes (down-growing) with 40/50° to 90° inclination, coated with laminated calcite. The stems are of a vew mm in inner diameter and coatings of a few mm thick. | Groups of down- growing stems laying parallel to flow | Hanging macrophy-tes (grasses) | Lbr, Lph. | Cascades in which hydrophilous hanging plants are coated with calcite. Fast progradation of upper fronts of cascades, which can form over-hangings (lighted areas). |
| /toherm tufas of: ophytes. Lbr js. 8C, 8E; 11G) iam to orange | Lenticular, hemi- domed bodies (up to 1 m high) resulting from moss layer stackings, 0.15 to 0.7 m thick and centimetres to metres wide. | Boundstones of moss layers, in which the caulidia are coated with calcite, commonly forming palisades parallel to the water flow, but also patches of intertwined moss ca. 15 cm high. | Parallel stacking of cm-thick layers building the phytoherm morphology. | Mosses | Lph, Lst 1, Lst 2. | Cascades, jumps, barrage- cascades, with preferential growth of mosses that are coated with calcite. |
| eleothems Lsp 3s 6D) aam to orange | Irregular rock bodies and stalactites. Outcrop reduced to a ca. 6-m high block. | Limestone composed of stalactite-shaped bodies, consisting of calcite-coated hanging stems, and irregular masses. | Overall structureless with few upgrowing stem boundstones and prograding bryophyte. | | Lph, Lst 2, Lbr. | Calcite precipitation in caves, behind cascades, on the walls and also on previously calcite-coated stems, which are further coated through dripping. |
| ssive and laminated rls. Mm, Mh gs. 7B, 9D, 9E, 9F; ht to dark grey and rt brown | Tabular beds, 0.04 to 0.20 m thick. Metres to decametres wide. | Fine siliciclastics (clay, silts) and lime mud. Microscopic and macroscopic coaly matter. | Structureless or with horizontal lamination | Carbonized plant debris and unidentifiable microscopic organic matter. | Sb, Lph and Coal | Settle-out in still water areas (ponds) in the channels and mostly on floodplains. |
| issive and laminated dstones. Fm, Fh gs. 9C, 9D, 9E, 9F; A, 10B, 10C; 111, 11J, () rk grey and brown to ck | Tabular and lenticular beds, up to 0.3 m thick. | Fine siliciclastics (clay, silts) and less abundant carbonate particles. | Commonly structureless, in some cases with horizontal lamination. | Occasional intraclasts and coaly plant debris. | Gm, Gr, Sr, Sh | Overbank deposits: settle-out in floodplains. |
| ndstones and nds with trough ss-stratification izontal lamination. Sr, Sh gs .6A, 6D; 9A, 9C; A, 10B, 10C) aam to light brown/ esam to light brown | Lenticular and tabular, 0.1 to 0.55 m thick, bodies, some with concave bases and flat tops. At places, grouped in sets up to 1.9 m thick. | Fine to coarse siliceous particles with scattered heterometric clasts consisting of Mesozoic limestone, quartz and tufa, supported by a matrix. The grains are rounded to subrounded. | Trough-cross stratification and lamination, in sets up to 0.25 m thick. Horizonal lamination. | Exceptionally, fragments of coated macrophytes (dm-long, phytoclasts) is recognized | En, Fh | Small sand bars and ripples in low energy channels. Sandy deposits in floodplain. |

| Facies and abundance (Figures) Colour | Geometry of deposits | Microstructure, texture and components | Sedimentary structures | Identifiable biological content | Common associated facies | Depositional sedimentary context |
|---|---|--|--|--|--------------------------------|---|
| Conglomerates and gravels. Gm, Gt ■ (Figs. 6A, 6D; 9A, 9B, 9C) Light brown and light grey-orange | Lenticular, channel- shaped bodies (concave base and flat top), 0.6 m thick and tabular bodies, from 1.7 to 3 m thick. | Clast supported. Varied nature of particles: Mesozoic limestones and detrital (of siliciclastic and carbonate particles) rocks; Quaternary limestones, commonly coarse phytoclasts and other intraclasts. Heteronetric, angular to rounded particles. Sandy-gravel matrix and minor or absent carbonate cement. They form gravelly fining-upward sequences. Clast imbrication Palaeocurrent: 150-180. | Structureless. In some cases with trough-cross stratification | Phytoclasts | Lph, Fm and St | Incision followed by gravel fill of fluvial channels during high discharge episods. |
| Organic-matter and organic matter-rich mud. C I (108, 78; 9E; 108,10C,10D; 11J, 11K) Dark grey and brown to black | Tabular and lenticular up to 0.1 m thick. Grouped in sets from 0.35 to 0.4 m thick | Microscopic and macroscopic carbonaceous matter. Humic and sapropelic, low-rank coal stages, sediments with high content in organic matter. | | Carbonaceous fragments of plants | Sb, Lb, and Lph | Almost quiet-water areas (stagnant or poorly drained ponds) that are site for microscopic plant remains or vegetal debris accumulation, with anoxia conditions at the bottom. |
| (■) Occasional ■ Minor ■ | Common mem Very cor | nmon ■■■■ Ubiquitous | | | | |

16





Fig. 11.— Photomicrographs of tufas and associated carbonate and siliciclastic fine facies: (A) Bioclastic limestone (Lb). Each 'grain' is a piece of grouped cyanobacteria filaments (micrites). (B) Slightly lithified carbonate sand and silt (SB). (C) Phytoclastic limestone (Lph), showing cross sections of calcite coated stems. (D) Cross sections of coated stem boundstone (Lst1). (E) Bush masses of cyanobacteria with micrite filaments coating on an up-growing stem. (F) SEM image of the laminated coating on a microscopic stem. Note alternating coarse and fine crystals. (G) Moss stems in a bryophyte boundstone (Lbr). Not high framework porosity. (H) Mixed siliciclastic and carbonate grains in sandstones. (I) Laminated siltstones. (J) Unsorted, mostly quartz grains in micritic matrix, with dark organic-rich lamina. (K) Siltstone with dark organic-rich laminae (L) SEM image. Kaolinite in a siltstone.



Fig. 11.— (Cont.)

to the interval between meters 7 to 12 (units 4 and 5) of section 3, approximately.

Thus, the deposits cropping out in the Los Santos studied area are relatively thinner compared to those in other areas such as Castielfabib (*e.g.* 77 m thick in section d; Fig. 3), in the upper reach along the Ebrón river Valley.

The lack of absolute dates prevents this study from precise correlation. It has to be considered that the depositional architecture and the lateral variations of facies in fluvial tufa systems are intrinsic characteristics that can make it difficult correlation throughout the basin. Nonetheless, the proposed correlation in this work seems plausible given the small distance between the studied areas and smooth geometry of deposits in the Los Santos outcrop. Correlation between the latter and the upstream area is established by mapping criteria through aerial photograph.

Sedimentology

A variety of sedimentary facies has been found (carbonate, detrital and peaty; Table 1 and Figs. 8, 9 and 10). The main mineralogy of the carbonate facies was calcite, as determined through microscopy and calcimetry analyses (see Materials and methods). In a few cases, these facies contain minor amounts of clay- to sand-size siliceous grains. A wide array of carbonate facies has been distinguished in the studied area based on texture and biotic composition (Table 1 and Fig. 8). The most abundant facies are the phytoclastic rudstones (Lph, Lphf), carbonate sands with gastropods and ostracods (Sb) and up-growing stem boundstones (Lst1). Less common are moss boundstones (Lbr), down-growing stem boundstones (Lst 2) and bioclastic limestones (Lb). In general, plant stems are coated with several concentric laminae (Fig. 11C, 11D), which in most cases contain bacterial evidence, *i.e.*, cyanobacterial fan- and bush-shaped calcite bodies, as well as isolated filament moulds (Fig. 11E, 11F). Most of these facies were formed in multiple sub-environments, except for the occasionally occurring curtains of hanging stems, which formed in waterfalls. For example, up-growing stems developed in fluvial banks, shallow pools and floodplains; phytoclasts were ubiquitous, thus phytoclastic rudstones are found in almost every sub-environment; bryophyte layers formed in waterfalls, barrages and jumps.



Figure 12.— Some of the most common facies associations (FAs) in the Los Santos area of the Ebrón river Valley. Explanation in the text.

Detrital (extraclastic) facies are characterized based on texture and sedimentary structures (Table 1 and Fig. 9). Conglomerates and gravels consist of angular to rounded, poorly sorted, carbonate and minor siliceous extraclasts, mainly from Mesozoic rocks, and at times including Quaternary tufa clasts, which together are embedded in a polymictic sandy-gravel matrix. They mostly form structureless deposits (Gm), but locally can show cross stratification (Gt). Sandstones and siltstones are also of polymictic nature, including variable amount of tufa intraclasts. All these clastic deposits occur at the base of the outcropping record and represent first incision and then deposition in low sinuosity channels during high energy events (Gm, Gt, St). Mudstones, consisting mostly of siliciceous grains (Fm, Fh), and marls (Mm) may be associated with thin peaty layers (facies C), giving evidence of periods of stagnant water on the floodplain and in ponds (Figs. 10; 11J, 11K).

Facies Associations (FA) and depositional interpretations

The sedimentary facies recognized in the Los Santos area of the Ebrón Valley are associated vertically into simple vertical sequences or facies associations (FAs) that recorded the sedimentary processes that occurred in a particular sedimentary area through time. In the field, five facies associations were recognized (Fig. 12).

Facies Association 1: Channel fill and floodplain passing to palustrine zones

The succession of gravels (Gm, locally Gt) followed by sands (St) and then fines with ripples, horizontal lamination or structureless (Sr, Sh, Sm) (Fig. 6A, 9A, 9B, 9C) in this FA represents a typical channel fill. The subsequent marly and carbonate sandy deposition with peaty sediment formed in a floodplain environment with stagnant pools. Subsequently, carbonate deposition became dominant in palustrine conditions, with extensive areas of submerged up-growing plants producing calcite-coated stems, later becoming boundstones and rudstones (Lst1, Lph), and in pools with sand and fine phytoclasts (Sb, Lphf) (Fig. 9D, 9F).

In brief, this sequence indicates incision periods of the fluvial channels followed by gravel fill during high discharge, then decreasing energy, ending with floodplain and carbonate palustrine zones, with shallow pools and slow-flowing water. Facies sequences comparable to FA 1 herein have been described at the initial stages of deposition in low- to moderate-slope carbonate fluvial systems in northeast Spain (Vázquez-Urbez *et al.*, 2012). Henchiri (2014) found macrophyte stem boundstones in palustrine facies associations of Quaternary fluvial tufa systems in southwestern Tunisia, similar to those herein described at the upper part of FA 1.

Two variations of FA 1 are distinguished based on the absence of the channel fill and floodplain deposits (FA 2) and the presence of significant deposits representing stagnant pools in the palustrine zones (FA 3).

Facies Association 2: Palustrine zones with pools

This FA, firstly with dominant calcite-coated up-growing stems and carbonate sands and bioclastic limestones in lateral relation, followed by phytoclastic rudstones, being the calcite-coated clasts originated from erosion of the palustrine zones (Fig. 7D, 7E), overall reflects a dominant low energy environment. These deposits are associated with extensive sandy and bioclastic limestone deposits formed in shallow slow-flowing and ponded areas along the river channel (pools) and mostly in the floodplain. The height and density of the plant moulds (facies Lst1) give account of the presence of thriving marshy vegetation (*e.g.*, reeds) and sluggish water areas throughout (Fig. 8B, 8D, 8F).

Pedley *et al.* (2003) described palustrine conditions with laterally related up-growing plants and laminated tufa deposits in Quaternary tufas in central Spain (Guadalajara province). Vázquez-Urbez *et al.* (2012) described similar facies associations in the Pleistocene, lower reach deposits of the Mesa River (northeast Spain).

Facies Association 3: Palustrine zones with stagnant pools

This FA is formed of calcite-coated up-growing stems and phytoclasts in lateral relation, followed by fine-grained phytoclast accumulation produced from breakage of calcite-coated hygrophytes of palustrine areas, together representing a palustrine environment. This is associated with massive lime mud deposits (Mm and Sb) with interbedded organic-rich layers, which resulted from fine carbonaceous debris settling-out in still water areas (stagnant ponds on floodplain) formed in low energy conditions (Fig. 7B; 9b, 9C, 9D). Pedley *et al.* (2003) described palustrine conditions with organic-rich mud accumulation in Quaternary tufas in central Spain (Guadalajara province).

Facies Association 4: Low-slope channel with small cascades and pools

Phytoclast accumulation (Lph), then up-growing stem deposits (Lst1), represent channel fill followed by low-discharge or intermittent current areas with growth of hygrophytes around which calcite precipitated then forming boundstones (Lst1), while some fragments would form phytoclastic deposits, then rudstones (Lph). These deposits would be site for cascades to form and for moss mats to develop ahead the up-growing stems (Fig. 8C). The progradation and aggradation of stacking moss layers, up-growing stems and phytoclasts would favour formation of small barrages that pooled water upstream, with accumulation of bioclastic lime mud in almost quiet-water areas upstream (as described by Pedley, 2009; Arenas-Abad et al., 2010; Toker, 2017). Therefore, FA 4 represents small moss mounds and related pool deposits along the streams.

Facies Association 5: Cascade and dammed areas

This FA is not common; the formation and accumulation of calcite-coated up-growing stems and phytoclasts, both in lateral relation, reflect palustrine conditions. This situation was followed by expansion of pooled areas in which gastropods thrived and lime mud accumulated (Sb and Lphf); then the upstream cascades with moss layers (Lbr) prograded into the dammed, pool areas. This FA 5 is similar to the upper half of FA 1, but adds the development of cascade deposits (Lbr, Lst2 and Lsp), which represent the occurrence of small knickpoints along the fluvial valley (*e.g.*, Pedley, 2009; Vázquez-Urbez *et al.*, 2012; Gradziński *et al.*, 2013).

Discussion

Proposal of a sedimentary facies model

The proposed sedimentation model was constructed based on the stratigraphic correlation and the various facies associations that resulted from progradation, aggradation and lateral migration of environments through time. The studied deposits represent the distal termination of a high-slope fluvial tufa system, in which the decreasing slope downstream favoured the development of palustrine areas, shallow ponded areas and small cascades. Moreover, the increase in width of the valley downstream favoured extensive development and preservation of the palustrine facies (*i.e.*, up-growing calcite-coated stem boundstone). Therefore, the model corresponds to a low-slope, wide stretch dominated by palustrine conditions at the end of a stepped, cascade-barrage fluvial system (Fig. 13).

This model includes detrital sediments (extraclasts) that were deposited in shallow channels during incision periods due to high water discharge events, leading to gravel and sand deposits. Typically, channel incision during high discharge occurred at the initial stages of the Middle-Late Pleistocene record and was followed by gravel and sand fill and then by floodplain deposits, at places with accumulation of fine-grained carbonaceous matter (FA 1). Afterwards, carbonate sedimentation turned to be dominant throughout. Most flat areas became then site for palustrine vegetation with sluggish water flowing across extensive areas. The flooded action from some high-energy episodes eroded the up-growing stem phytoherms and associated deposits (e.g., carbonate sands) over the palustrine zones, producing phytoclasts that were deposited along the channels (e.g., at the beginning of FA 2 and 3) and on the palustrine areas. Some phytoclastic accumulations favoured the formation of small cascades and barrages-cascades along the channel, with deposition of fine sediment (i.e., carbonate sand and granule size) in the upstream dammed areas and moss lavers downstream (FA 4). Progradation of these cascades and barrages-cascades structures gave rise to small hanging calcite-coated stem boundstones (e.g. as in FA 5). Hydrophilous vegetation and pooled areas with sandy sediment became dominant downstream in flat zones



Figure 13.— Sedimentary facies model proposed for the Ebrón river Valley during the Middle - Late Pleistocene, based on original data from this study and data from upstream deposits provided by Lozano *et al.* (2012). Mirador and Cascade correspond to sections c and d in Figures 2 and 3 of this work.

(FA 2 and 3), where aggradation of carbonate sand and lime mud in slow flowing and ponded areas occurred during low energy discharges (FA 2, 3 and 5). In this context, the hygrophilous plants were partially to fully submerged, then becoming coated with calcite and transformed into boundstone of up-growing stems. Also present is the abundant phytoclastic rudstone, which originated from the breakage of calcite-coated hydrophytes and broken stems accumulated in the palustrine environments. Water stagnation of some zones in these areas favoured accumulation of marly, silty and sandy sediment and preservation of peaty matter (FA 3).

Factors controlling extensive palustrine deposition and preservation

Considering the large-scale sedimentary context of the Ebrón Valley, the different pre-Quaternary car-

bonate and non-carbonate rocks are incised by the present river as it flows down the decreasing slope gradient. There is a remarkable contrast between the upstream and downstream sedimentological features in the Pleistocene outcrops. The large cascade-barrage structures (formed of moss and stromatolite bioherms) and associated thick dam deposits upstream (consisting of carbonate sands and phytoclastic rudstones), e.g., near Castielfabib (as described in Lozano et al., 2012, and Sancho et al., 2015), became much less prominent downstream (e.g., near Los Santos). There, cascade-barrage structures were smaller and overall "small-slope and slow-water facies" were dominant (e.g., carbonate sands and silts, phytoclastic rudstones and stem phytoherms). Interestingly, stromatolites, which commonly form in fast-flowing water areas along moderate to high slope zones (e.g., Violante et al., 1994; Arenas et

al., 2014b), are absent in the Los Santos area of the Ebrón Valley. Moreover, most moss mounds form discrete bodies that represent small jumps (Fig. 5). Another remarkable attribute in the Los Santos study area is the lack or limited presence of features denoting large or deep erosional processes within the tufa sequence, which supports deposition in overall slow to moderate flow condition.

These depositional changes coincide with a general decrease in slope and an increase in width downstream through the valley during the Pleistocene. This change was conditioned by variations of bedrock lithology, from Mesozoic carbonate rocks upstream to Neogene alluvial rocks downstream (*e.g.*, as shown in Fig. 2). The gentle sloping topography of the Los Santos area and the lack of vigorous erosional processes at the distal termination of the fluvial system enabled a dominant palustrine condition to exist on the sluggish streams, along stream banks and in pools within wide floodplains.

The Los Santos tufa sequence is much thinner (up to 19 m) than the Castielfabib sequence (up to 77 m), which is consistent with the distal deposition from the carbonate source (springs upstream), leading to reduction of calcite precipitation downstream, due to the decrease of the dissolved calcium carbonate content and/or the diminishing mechanical CO₂-loss, related to lesser water turbulence. This feature has been shown in some modern fluvial tufa systems (Arenas et al., 2015). Remarkable is the fact that the present day water composition of the Ebrón River shows, mostly in the downstream area, minor decreasing trends in Ca content and alkalinity values, but the values of the Saturation Index with respect to calcite usually remains higher than +0.6, suggesting the existence of tufa sedimentation in the distal part of the river, though reduced compared to upstream deposition rates (Arenas et al., 2015). Moreover, present day sedimentation studies indicate that the tufa deposition rates in each fluvial subenvironment of the Ebrón River were mainly controlled by the CO₂-outgassing intensity linked to local flow conditions and the biological substrate type (Arenas et al., 2015). In the Pleistocene study case, a decrease in CO₂-outgassing intensity would be expected, as the area corresponded to the downstream, low-slope area. As a matter of the fact, thickness of deposits on tablets monitored every six months along that river also showed decreasing depositional rates downstream, coinciding with the area of Los Santos. Additional water inputs through springs that introduce CO_2 in the carbonate system may cause decreases in calcite precipitation, as in the case of the present Ebrón River (Arenas *et al.*, 2015). This type of water input was occasional in the downstream stretch. In the Pleistocene, although spring CO_2 -inputs may have accounted for the small tufa accumulation at the downstream part of the system, this type of inputs is not expected to have been dominant, given the extensive palustrine tufa deposits. Thus, springs, if present, were small or occasional.

Many other ancient sedimentary fluvial systems with slope and facies changes along the valley path have been found in the Quaternary record (*e.g.*, Violante *et al.*, 1994; Pedley *et al.*, 1996; Arenas *et al.*, 2014a; Capezzuoli *et al.*, 2014; Huerta *et al.*, 2016; Toker, 2017). Several other Quaternary examples with palustrine environments come from central Italy (Buccino *et al.*, 1978), Israel (Heimann & Sass, 1989), central Spain (Pedley *et al.*, 2003), southern Turkey (Özkul *et al.*, 2010) and southwestern Tunisia (Henchiri, 2014). However, situations with extensive low-slope palustrine tufa areas at the most downstream fluvial stretch, as in the case study of Los Santos, are not so commonly preserved.

Arenas *et al.* (2014a) described a moderate-slope fluvial tufa model for Holocene deposits in the Iberian Ranges in which some portions with dominant palustrine facies could be similar to those in the Los Santos studied example. Thick palustrine deposits have also been described in the lower reach of the Pleistocene Mesa River (Váquez-Urbez *et al.*, 2012). Henchiri (2014) related the dominant palustrine conditions of Holocene tufas in southwestern Tunisia to bedrock configuration and the flat topography of the area where the springs emerged, prone to form a marshy context.

In the Los Santos studied system, the large dammed areas, opposed to minor and small cascades-barrages, formed as a result of gentle gradient in the wider valley, thus vertical growth of barrages was limited, while favouring lateral migration of the fluvial environment. Stagnant conditions in the pooled areas could be established due to the likely long periods without water renewal and lack of vigorous flow, which together favoured accumulation and preservation of organic matter such as peat (*e.g.* as described by Pedley *et al.*, 2003; Arenas *et al.*, 2014a; Henchiri, 2014).

The palustrine tufa of the Ebrón River is a typical example illustrating the distal evolution of a carbonate-rich riverine environment in a wide low-layering area that, in the downflow direction, progressively reduces or stops its capacity to precipitate calcite due to the decrease of the dissolved calcium carbonate and/or the diminishing mechanical CO₂-loss, related to lesser water turbulence in overall low-slope surfaces. In other settings, this calcite precipitation reduction has been related to the system entering other hydrological system with different hydro-geochemical characteristics (see Toker, 2017). In these settings, carbonate deposits are rapidly replaced by detrital tufa or mixed clastic successions (Ortiz et al., 2009; Martini & Capezzuoli, 2014). However, this is not the case of the Pleistocene example studied herein.

Together, the above discussion indicates the complex interplay of factors that control fluvial tufa deposition (geology, topography, hydrology, hydrochemistry, biology, climate; see Goudie *et al.*, 1993; Pedley *et al.*, 2003; Pentecost, 2005; Valero Garcés *et al.*, 2008; Arenas-Abad *et al.*, 2010). As cited above, the factors that favour the formation of tufa palustrine systems are: the reduced slope and large amplitude of the sedimentary substrate, the high saturation of water in calcium carbonate and the reduced and slow water level changes, along with the absence of strong erosional processes.

Subsidence is a principal factor that favours accumulation and preservation of different types of deposits. In the investigated environment, for instance, thick tufa, oncolite-bearing and bioclastic limestones formed in the middle-late Miocene of the Ebro Basin; thickness and preservation were clearly linked to subsidence induced by evaporite-solution of underlying bedrocks (Arenas *et al.*, 2000). In this case, the corresponding beds showed typical geometry and thickness variations. Similarly, thick and varied facies deposits formed westward in the Ebro Basin, in relation to subsidence associated to a blind thrust rooted in the Iberian Range during the middle-late Miocene (Vázquez-Urbez *et al.*, 2013). However, thick dominantly palustrine tufa successions preserved in basins affected by tectonic activity and subsidence have been reported only in a few cases (Ellera Basin; Pazzaglia *et al.*, 2013).

Due to the concurrence of such varied conditions, extensive areas of palustrine tufa at the downstream areas of fluvial systems form only rarely and related to local situations. For instance, in arid conditions (Ben Younes tufa - Gafsa area, Tunisia) Henchiri (2014) described extensive palustrine tufa deposits related to repeated occurrence of springs able to lead supersaturated waters. Tufa deposits can also represent the distal portion of thermal systems, where typical travertine facies are transitional to cooler, plant-rich tufa facies and especially of suitable environments as lakes, alluvial plains or marshes (Della Porta, 2015; Della Porta *et al.*, 2017; Brogi *et al.*, 2017; Mancini *et al.*, 2019; Mohammadi *et al.*, 2020).

In brief, from the above discussion, the factors that favour the formation of tufa palustrine systems are: the reduced slope and large width of the sedimentary substrate, the water saturation in calcium carbonate and the reduced and slow water level changes, along with the absence of strong water discharge provoking erosion. Preservation is expected to be greatly affected by subsidence, as in any other subaerial contexts. Whether subsidence could control the characteristics of the studied palustrine system in the Ebrón valley is unknown.

Conclusions

The Pleistocene Los Santos studied deposits represent the distal termination of a high-gradient fluvial tufa system in a wide low-layering area with typical features of the palustrine environment, with dominant up-growing stem boundstones and carbonate sand and silt deposits. This extensive area was close to the Ebrón river entering the main or trunk river (Turia River, southeastern Iberian Range, Spain).

Five fundamental facies associations were recognized: (FA 1) Channel fill and floodplain passing to palustrine zones; (FA 2) Palustrine zones with pools; (FA 3) Palustrine zones with stagnant ponds; (FA 4) Low-slope channel with small cascades and pools; (FA 5) Cascade and dammed areas.

The sedimentary facies model proposed in this work represents a carbonate fluvial sedimentary sys-

tem predominantly developed along the longitudinal profile and with limited lateral extension due to the surrounding relief, conditioning the river's migration path. The Los Santos area developed downstream of a stepped fluvial stretch. Bryophyte boundstones (Lbr) formed in small cascades, but were not common due to the low gradient, in contrast to pooled areas and extensive floodplain, hence with a dominant palustrine environment, with abundant carbonate sands (Sb), up-growing stem boundstones (Lst 1) and phytoclastic limestone (Lph). These conditions are consistent with the absence of stromatolites (Ls), typical of high-energy zones in upstream zones.

Bedrock lithology conditioned the slope decrease and the widening of the valley downstream. The occurrence of an extensive low-gradient area with stable water level and absence of strong erosional processes favoured the development of hydrophilous plants, shallow ponds with fine deposition and accumulation of organic matter, as well as the preservation of the correspondent deposits.

The general thinner tufa and minor clastic deposits in the studied area (up to 19 m) respect to the upstream deposits (up to 77 m) of the same fluvial system was linked to the distal deposition from the carbonate source (springs from carbonate aquifer), leading to reduction of dissolved calcium and bicarbonate contents downstream, and to the diminishing mechanical CO_2 -degassing in the low-gradient environments. Similar conditions occur at present in the Ebrón River.

ACKNOWLEDGEMENTS

This work was partly supported by an Erasmus+ grant in the frame of the European agreement between the Universities of Perugia (Italy) and Zaragoza (Spain). The "Servicios de Apoyo a la Investigación" of the University of Zaragoza provided rock samples and microscope preparations from material of project CGL2013-42867-P of the Spanish Government. The Department of Earth Sciences (Division of Stratigraphy and Sedimentology) of the University of Zaragoza offered their facilities to this work to realize laboratory analysis in the best possible way. Ildefonso Armenteros and an anonymous reviewer greatly contributed to improve the manuscript. This work is dedicated to our colleague Carlos Sancho Marcén, who died in February 2019. His enthusiasm for Quaternary tufas led us to continue exploring new fluvial systems.

References

- Álvaro, M. & 38 authors (1994). Mapa Geológico de la Península Ibérica, Baleares y Canarias. Scale 1:1,000,000. Instituto Tecnológico Geominero de España and Instituto Geológico e Mineiro de Portugal. Madrid.
- Arenas, C.; Gutiérrez, F.; Osácar, C. & Sancho, C. (2000). Sedimentology and geochemistry of fluvio-lacustrine tufa deposits controlled by evaporite solution subsidence in the central Ebro Depression, NE Spain. Sedimentology, 47: 883-909. https://doi.org/10.1046/ j.1365-3091.2000.00329.x
- Arenas-Abad, C.; Vázquez-Urbez, M.; Pardo-Tirapu, G. & Sancho-Marcén, C. (2010). Fluvial and Associated Carbonate Deposits. In: Carbonates in continental setting (Alonso-Zarza, A.M. & Tanner, L.H., Eds.), Developments in Sedimentology, Elsevier, 61: 133-170. https://doi.org/10.1016/S0070-4571(09)06103-2
- Arenas, C.; Vázquez-Urbez, M.; Pardo, G. & Sancho, C. (2014a). Sedimentology and depositional architecture of tufas deposited in stepped fluvial systems of changing slope: Lessons from the Quaternary Anamanza valley (Iberian Range, Spain). Sedimentology, 61: 133-171. https://doi.org/10.1111/sed.12053
- Arenas, C.; Vázquez-Urbez, M.; Auqué, L.; Sancho, C.; Osácar, C. & Pardo, G. (2014b). Intrinsic and extrinsic controls of spatial and temporal variations in modern fluvial tufa sedimentation: A thirteen-year record from a semi-arid environment. Sedimentology, 61: 90-132. https://doi.org/10.1111/sed.12045
- Arenas, C.; Auqué, L.; Osacar, M.C.; Sancho, C.; Vázquez-Urbez, M. & Pardo, G. (2015). Current tufa sedimentation in a high discharge river: A comparison with other synchronous tufa records in the Iberian Range (Spain). Sedimentary Geology, 325: 132-157. https://doi.org/10.1016/j.sedgeo.2015.05.007
- Auler, A.S. & Smart, P.L. (2001). Late Quaternary paleoclimate in semiarid northeastern Brazil from U-series dating of travertine and water-table speleothems. Quaternary Research, 55: 159-167. https://doi. org/10.1006/qres.2000.2213
- Brogi, A.; Capezzuoli, E.; Kele, S.; Baykara, M.O. & Shen, C-C. (2017). Key travertine tectofacies for neotectonics and palaeoseismicity reconstruction: effects of hydrothermal overpressured fluid injection. Journal of the Geological Society, 174(4): 679-699. https:// doi.org/10.1144/jgs2016-124
- Buccino, G.; D'Argenio, B.; Ferreri, V.; Brancaccio, L.; Panichi, C. & Stanzione, D. (1978). Il travertini della bassa Valle del Tanagrio (Campania): Studio geomorphologico, sedimentologico e geochimico. Bolletino della Societá Geologica Italiana, 97: 617-646.

- Capezzuoli, E.; Gandin, A. & Sandrelli, F. (2010). Calcareous tufa as indicators of climatic variability: A case from the Southern Tuscany (Italy). In: Tufas, Speleothems and Stromatolites: Unravelling the physical and microbial controls (Pedley, M. & Rogerson, M., Eds). Geological Society, London, Special Publications, 336: 263-281. https://doi.org/10.1144/SP336.14
- Capezzuoli, E.; Gandin, A. & Pedley, M. (2014). Decoding tufa and travertine (freshwater carbonates) in the sedimentary record: The state of the art. Sedimentology, 61: 1-21. https://doi.org/10.1111/sed.12075
- Cremaschi, M.; Zerboni, A.; Spotl, C. & Felletti, F. (2010). The calcareous tufa in the Tadrart Acacus Mt. (SW Fezzan, Libya). An early Holocene palaeoclimate archive in the central Sahara. Palaeogeography, Palaeoclimatology, Palaeoecology, 287: 81-94. https://doi. org/10.1016/j.palaeo.2010.01.019
- Della Porta, G., (2015). Carbonate build-ups in lacustrine, hydrothermal and fluvial settings: Comparing depositional geometry, fabric types and geochemical signature. In: Microbial Carbonates in Space and Time: Implications for Global Exploration and Production (Bosence, D.W.J.; Gibbons, K.A.; Le Heron, D.P.; Morgan, W.A.; Pritchard, T. & Vining, B.A., Eds.), Geological Society, London, Special Publications, 418: 17-68. https://doi.org/10.1144/SP418.4
- Della Porta, G.; Croci, A.; Martini, M. & Kele, S. (2017). Depositional architecture, facies character and geochemical signature of the Tivoli travertines (Pleistocene, Acque Albule Basin, Central Italy). Rivista Italiana di Paleontologia e Stratigrafia, 123: 487-540.
- Durán, J.J. (1989). Geocronología de los depósitos asociados al karst en España. In: El karst en España (Durán, J.J. & Martínez, J. (Eds.). Monografías Sociedad Española de Geomorfología, 4: 243-256.
- Freytet, P. & Plaziat, J.-C. (1982). Continental Carbonate Sedimentation and Pedogenesis -Late Cretaceous and Early Tertiary of Southern France. In: Contributions to Sedimentology (Purser, B.H., Ed.), Springer-Verlag, Stuttgart, 12: 213 pp.
- Gibbard, P.L.; Boreham, S.; Cohen, K.M. & Moscariello, A. (2005). Global chronostratigraphical correlation table for the last 2.7 million years. Boreas, 34.
- Goudie, A.S.; Viles, H.A. & Pentecost, A. (1993). The late-Holocene tufa decline in Europe. The Holocene, 3(2): 181-186. https://doi. org/10.1177/095968369300300211
- Gradziński, M.; Hercman, H.; Jaskiewicz, M. & Szczurek, S. (2013). Holocene tufa in the Slovak Karst: facies, sedimentary environments and depositional history. Geological Quarterly, 57 (4): 769-788. https://doi. org/10.7306/gq.1131

- Heimann, A. & Sass, E. (1989). Travertines in Northern Hula Valley, Israel. Sedimentology, 36: 95-108. https://doi.org/10.1111/j.1365-3091.1989.tb00822.x
- Henchiri, M. (2014). Quaternary paludal tufas from the Ben Younes spring system, Gafsa, southwestern Tunisia: interactions between tectonics and climate. Quaternary International, 338: 71-87. https://doi. org/10.1016/j.quaint.2013.12.024
- Henning, G.J.; Grün, R. & Brunnacker, K. (1983). Speleothems, travertines and paleoclimates. Quaternary Research, 20: 1-29. https://doi.org/10.1016/0033-5894(83)90063-7
- Huerta, P.; Armenteros, I.; Merino Tomé, Ó.; Rodríguez Gonzálvez, P.; Silva, P.G.; González Aguilera, D. & Carrasco-García, P. (2016). 3-D modelling of a fossil tufa outcrop. The example of La Peña del Manto (Soria, Spain). Sedimentary Geology, 333: 130-146. https://doi.org/10.1016/j.sedgeo.2015.12.013
- Lozano, M.V.; Sancho, C.; Arenas, C.; Vázquez-Urbez, M.; Ortiz, J.E.; Torres, T.; Pardo, G.; Osacar, M.C. & Auqué, L. (2012). Analisis preliminar de las tobas cuaternarias del Río Ebrón (Castielfabib, Valencia, Cordillera Ibérica). Geogaceta, 51: 51-54.
- Mancini, A.; Capezzuoli, E.; Erthal, M. & Swennen, R. (2019). Hierarchical approach to define travertine depositional systems: 3D conceptual morphological model and possible applications. Marine and Petroleum Geology, 103: 549-563. https://doi.org/10.1016/j. marpetgeo.2019.02.021
- Martín Algarra, A.; Martín-Martín, M.; Andreo, B.; Julià, R. & González-Gómez, C. (2003). Sedimentary patterns in perched spring travertines near Granada (Spain) as indicators of the paleohydrological and paleoclimatological evolution of a karst massif. Sedimentary Geology, 161: 217-228. https://doi. org/10.1016/S0037-0738(03)00115-5
- Martini, I. & Capezzuoli, E. (2014). Interdigitated fluvial clastic deposits and calcareous tufa testifying an uplift of the catchment area: An example from the Pianizzoli area (southern Tuscany, Italy). Sedimentary Geology, 299: 60-73. https://doi.org/10.1016/j.sedgeo.2013.11.001
- Miall, A.D. (1978). Lithofacies Types and Vertical Profile Models in Braided River Deposits: A Summary. In: Fluvial Sedimentology (Miall, A.D., Ed.), Canadian Society of Petroleum Geologists, Memoir 5, Calgary, 597-604.
- Moeyersons, J.; Nyssen, J.; Poesen, J.; Deckers, J. & Haile, M. (2006). Age and backfill/overfill stratigraphy of two tufa dams, Tigray Highlands, Ethiopia: Evidence for Late Pleistocene and Holocene wet conditions. Palaeogeography, Palaeoclimatology, Pala-

eoecology, 230: 165-181. https://doi.org/10.1016/j. palaeo.2005.07.013

- Mohammadi, Z.; Claes, H.; Capezzuoli, E.; Mozafari, M.; Soete, J.; Aratman, C. & Swennen, R. (2020). Lateral and vertical variations in sedimentology and geochemistry of sub-horizontal laminated travertines (Çakmak quarry, Denizli Basin, Turkey). Quaternary International, 540: 146-168. https://doi.org/10.1016/j. quaint.2018.11.041
- Ortiz, J.E.; Torres, T.; Delgado, A.; Reyes, E. & Díaz-Bautista, A. (2009). A review of the Tagus river tufa deposits (central Spain): Age and palaeoenvironmental record. Quaternary Science Reviews, 28: 947-963. https://doi.org/10.1016/j.quascirev.2008.12.007
- Özkul, M.; Gökgöz, A. & Horvatincic, N. (2010). Study from the Denizli Province, Western Turkey springline tufa deposits and associated spring waters: A case study from the Denizli Province, Western Turkey. In: Tufas and Speleothems: Unravelling the Microbial and Physical Controls (Pedley, H.M. & Rogerson, M., Eds.), Geological Society, London, Special Publications, 336: 245-262. https://doi.org/10.1144/SP336.13
- Pazzaglia, F.; Barchi, M.R.; Buratti, N.; Cherin, M.; Pandolfi, L. & Ricci, M., (2013). Pleistocene calcareous tufa from the Ellera basin (Umbria, central Italy) as a key for an integrated paleoenvironmental and tectonic reconstruction. Quaternary International, 292: 59-70. https://doi.org/10.1016/j.quaint.2012.11.020
- Pedley, H.M. (2009). Tufas and travertines of the Mediterranean region: a testing ground for freshwater carbonate concepts and developments. Sedimentology, 56: 221-246. https://doi.org/10.1111/j.1365-3091.2008.01012.x
- Pedley, H.M., Andrews, J., Ordóñez, S., González-Martín, J.A., García Del Cura, M.A. & Taylor, D. (1996). Does climate control the morphological fabric of freshwater carbonates? a comparative study of Holocene barrage tufas from Spain and Britain. Palaeogeography, Palaeoclimatology, Palaeoecology, 121: 239-257. https:// doi.org/10.1016/0031-0182(95)00080-1
- Pedley, H.M.; Ordóñez, S.; González Martín, J.A. & García del Cura, M.A. (2003). Sedimentology of Quaternary perched springline and paludal tufas: Criteria for recognition, with examples from Guadalajara

Province, Spain. Sedimentology, 50: 23-44. https:// doi.org/10.1046/j.1365-3091.2003.00502.x

- Pentecost, A. (2005). Travertine. Springer-Verlag, Berlin, 445 pp.
- Sancho, C.; Arenas, C.; Vázquez-Urbez, M.; Pardo, G.; Lozano, M.V.; Peña-Monné, J.L.; Hellstrom, J.; Ortiz, J.E.; Osácar, M.C.; Auqué, L. & Torres, T. (2015). Climatic implications of the quaternary fluvial tufa record in the NE Iberian Peninsula over the last 500 ka. Quaternary Research, 84 (3): 398-414. https://doi. org/10.1016/j.yqres.2015.08.003
- Toker, E. (2017). Quaternary Fluvial Tufas from Sarikavak Area, Denizli, Southwestern Turkey: Facies and depositional systems. Quaternary International, 437: 37-50. https://doi.org/10.1016/j.quaint.2016.06.034
- Valero Garcés, B.L.; Moreno, A.; Navas, A.; Mata, P., Machín, J.; Delgado Huertas, A., González Sampériz, P., Schwalb, A.; Morellón, M.; Cheng, H. & Edwards, R.L. (2008). The Taravilla lake and tufa deposits (Central Iberian Range, Spain) as palaeohydrological and palaeoclimatic indicators. Palaeogeography, Palaeoclimatology, Palaeoecology, 259: 136-156. https://doi. org/10.1016/j.palaeo.2007.10.004
- Vázquez-Urbez, M.; Arenas, C. & Pardo, G. (2012). A sedimentary facies model for stepped, fluvial tufa systems in the Iberian range (Spain): The quaternary Piedra and Mesa valleys. Sedimentology, 59: 502-526. https://doi.org/10.1111/j.1365-3091.2011.01262.x
- Viles, H.A. & Pentecost, A. (2007). Tufa and travertine. In: Geochemical Sediments and Landscapes (Nash, D. & McLaren, S., Eds.). Blackwell Publishing, Oxford, 173-199. https://doi.org/10.1002/9780470712917.ch6
- Viles, H.A.; Taylor, M.P.; Nicoll, K. & Neumann, S. (2007). Facies evidence of hydroclimatic regime shifts in tufa depositional sequences from the arid Naukluft Mountains, Namibia. Sedimentary Geology, 195: 39-53. https://doi.org/10.1016/j.sedgeo.2006.07.007
- Violante, C.; Ferreri, V.; D'Argenio, B. & Golubic, S. (1994). Quaternary travertines at Rochetta a Volturno (Isernia, Central Italy). Facies analysis and sedimentary model of an organogenic carbonate system. PreMeeting Fieldtrip Guidebook, A1. International Association of Sedimentologist, Ischia '94, 15th regional meeting, Italy, 3-23.